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(54) Title: POLYOLEFIN FILM, TAPE OR YARN

(57) **Abstract:** The invention is directed to monoaxially drawn polyolefin multilayer film, tape or yarn of the AB or ABA type, having a stretch ratio of more than 12, having an E-modulus of at least 10GPa, substantially consisting of a central layer (B) of a polyolefin selected from polyethylene and polypropylene, and one or two other layers (A) of a polyolefin from the same class as the material of the central layer B, the DSC melting point of the material of the said other layers (A) being lower than the DSC melting point of the material of the said central layer (B), wherein the central layer (B) is between 50 and 99 wt.% of the material and the other layers (A) between 1 and 50 wt.%. The present invention further relates to a method of manufacturing such a tape, film or yarn.

Polyolefin film, tape or yarn

The invention is directed to a polypropylene multilayer film, tape or yarn, suitable for producing reinforcing woven and non-woven type materials, especially for strengthening and/or stiffening of products. Polyolefin films of mono- or multiplayer type are generally produced by blown film or cast film extrusion. At some stage of the production process the material can be stretched in order to increase the strength and stiffness of the material.

5 Polyolefin tapes and yarns are generally produced from polyolefin films of mono- or multilayer type, by cutting the film to the desired width. At some stage of the production process the material can be stretched in order to 10 increase the strength and stiffness of the material.

US-A 5,578,370 describes a thermoplastic composite material formed of a polypropylene film that is coated with a layer of an ethylene copolymer further comprising propylene units. The coated layer has a lower softening point than the polypropylene core. The publication describes the 15 stretching of the material to a draw ratio of 20:1 in a hot air oven. The examples indicate that composites of the material may have a mean tensile modulus of elasticity of up to 2.5 GPa.

JP-A 2000-8244 describes a flat yarn cloth for reinforcing laminated layers, prepared from a composite yarn of the ABA type, wherein the B layer is 20 a polypropylene and the A layers are based on an ethylene- α -olefin copolymer or a blend of two ethylene- α -olefin copolymers. The yarns are produced by co-extruding the two materials, slitting the film and stretching it to a stretch ratio of 3-12. After weaving, the material is heat treated to weld the yarns together.

25 EP-A 336,210 describes a three-ply drawn polyolefin laminate comprising a core layer of polypropylene and/or LLDPE and top layers from butene-1 polymers. The material can be used in the packaging area. This material has poor mechanical properties.

EP-A 776,762 describes a polyolefin tape or yarn based on a co-extruded polyolefin material, having a stretch ratio of 6 to 10. This material is described as being suitable for preparing all kinds of cloths, strappings and the like.

5 Although the properties of the material according to the above citations are quite good, especially with respect to tensile strength, there is a need for further improvement. It is a first object of the present invention to provide a tape or yarn having improved mechanical properties.

10 In composite materials yarns and cloths are often used for reinforcing. Most commonly used are glass fibre materials. However, glass fibre materials have the disadvantage that they make it very difficult to recycle the materials in which they are incorporated. It would be very useful if the glass fibres could be replaced by polymeric fibres or other polymeric reinforcement components, thereby making it easier to recycle the composite materials. One of the strong advantages of glass fibres reside in the stiffness thereof, which is generally one of the weak aspects of polymeric fibres or other reinforcement components. Accordingly, it is a further object of the invention to provide polymeric materials that have sufficient stiffness to be able to replace glass fibres in composite materials.

20 With respect to recycling of the products produced from polyolefin films, tapes and yarns it would be an advantage if all components of the material could be classified as the same material, such as polypropylene or polyethylene (including copolymers thereof wherein propylene respectively ethylene forms the majority of the monomeric units). The advantage thereof would be that the resulting recycled material would still be one material, instead of a blend of various components (no contamination).

25 The present invention is directed to a monoaxially drawn polyolefin multilayer film, tape or yarn of the AB or ABA type having a stretch ratio of more than 12, having an E-modulus of at least 10 GPa, substantially consisting of a central layer (B) of a polyolefin selected from polyethylene and

polypropylene, and one or two other layers (A) of a polyolefin from the same class as the material of the central layer B, the DSC melting point of the material of the said other layers (A) being lower than the DSC melting point of the material of the said central layer (B), wherein the central layer (B) is 5 between 50 and 99 wt.% of the material and the other layers (A) between 1 and 50 wt.%.

Surprisingly it has been found that this multilayer material (also referred to as laminate) has excellent properties with respect to mechanical strength, stiffness and the like. Because of its composition, it can be qualified 10 as a mono-component material being either polyethylene or polypropylene, which is an advantage in recycling. More in particular it is possible to recycle production scrap as part of the central layer component. Further, in view of the requirements to manufacturers of consumer goods, such as cars and the like, concerning the possibility of recycling of the components after the useful life of 15 the product, it is important that components consist of one class of material only.

The E-modulus as used herein is the value as measured by ISO 527.

By combining the material composition of the laminate (film/tape/yarn) with the extremely high total stretch ratio, more than 12, 20 preferably more than 15, such as at least 20 and even up to 50 or more, a material has been created that can be used advantageously for all kinds of reinforcements, that can replace e.g. glass fibres in various reinforcing applications and that can be used in various higher temperature applications, such as automotive or aerospace applications. In general, the material of the 25 invention especially suitable for (lightweight) construction applications, high pressure applications and medical applications. It is possible to apply the material in the construction of houses, ships, cars, and the like, but also as reinforcement in high pressure parts, such as tubes (for oil production and the like), or in the production of orthoses.

In the context of this invention, the material has been defined as meeting a minimum level of the total stretch ratio (TSR). TSR is defined as the degree of stretching from an isotropic melt to the final tape or film. This is at least in part defined by the difference in speed between the stretch rollers. The 5 actual value of the TSR can be determined from the birefringence and/or the E-Modulus of the final film, tape or yarn (in stretching direction). The TSR applies especially to the central layer, which preferably is a highly crystalline material. The material of the other layer will generally be less crystalline. The function of the other layer is especially the provision of the possibility to weld 10 the films, tapes, fibres or yarns together when a woven, non-woven or staple/stack of the material is heat treated.

The basic materials to be used in the production of the film, tape or yarn according to the invention are polypropylene or polyethylene.

In case of the use of polypropylene as the material for the film, tape, 15 yarn or fibre, the material for the central, or core, layer B will preferably be a homopolypropylene, preferably having a relatively high molecular weight, such as a weight average molecular weight (MW) of at least 250 000 g/mol, as determined gel permeation chromatography (GPC), and a melting temperature of at least 160°C. It is to be noted that the central layer preferably consists of 20 one material only, but that in case of recycle of production scrap, minor amounts of the material of the other layer may also be present in the core layer. This will generally not exceed 10 wt.%.

In an embodiment wherein the core layer (B) is a polypropylene, the material of the outer layers in this embodiment is, as indicated above, also a 25 polypropylene, preferably a copolymer of propylene with ethylene or another α -olefin. An important aspect thereof is that the softening point of the material, generally indicated by the DSC melting point as defined in ISO 11357-3 is lower than the softening point of the central layer, the difference being at least 10°C. The maximum difference between softening points of the layer B and the 30 layer(s) A is not particularly critical. For practical reasons, the difference will

usually be less than about 70 °C. Very good results have inter alia been achieved with a film, tape or yarn wherein the difference in softening points is in the range of 15-40 °C.

Very good results have been achieved with a random copolymer,

5 such as a propylene-ethylene random copolymer, as the outer layer(s) A. Instead of a copolymer or in combination therewith, a polyolefin, preferably a polypropylene homopolymer or polypropylene copolymer, prepared by making use of a metallocene catalyst is used as the outer layer(s) A. Particular good results have been achieved with such a metallocene based statistical polymer.

10 A suitable example of a metallocene is rac-[Me₂Si(2-Me-4-(1-Naphtyl)Ind)2]ZrCl₂ H. (described in H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. 107 (1995) 1255 and in W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907).

As the product of the invention is generally used in a form where the

15 films, tapes or fibres are at angle to each other (woven, non-woven materials), the outer layer makes it possible to heat treat the woven, stacked or stapled material, thereby welding together the individual films/fibres/yarns or tapes to create a composite material (e.g. a woven material) of very high structural integrity. By selecting the softening point at a sufficiently large distance from

20 the softening point of the central layer, it is possible to have a heat treatment which does not impair the properties of the material itself.

In an embodiment of the invention, the outer layer or layers A at least consist of a ethylene propylene copolymer, having an ethylene content of between 75 mol % and 99 mol % and a propylene content of between 1 and 25 mol %. Particular good results have been achieved with such an outer layer or layers in an embodiment wherein the central layer B is a polyethylene.

It is preferred to use a propylene ethylene copolymer, having an ethylene content of between 1 and 25 mol.% and a propylene content of between 75 mol % and 99 mol %, as the material for the outer layers A, in

30 particular if the central layer is a polypropylene. Such a copolymer (as outer

layer(s) A), in particular such a random copolymer, has been found to adhere highly satisfactorily to the central layer. Further a composite of tape, yarn or film comprising such a copolymer has been found to have a very good strength, impact resistance and abrasion resistance. It is also possible to use blends of 5 two of these materials.

In case of the use of polyethylene, basically the same considerations apply. As the central layer an HDPE is preferably used, i.e. a polyethylene having a density of at least 950 kg/m³. The weight average molecular weight (MW), as determined by GPC, is preferably at least 250 000 g/mol and the 10 melting point is 130°C or higher. It is to be noted that the central layer preferably consists of one material only, but that in case of recycle of production scrap, minor amounts of the material of the other layer may also be present in the core layer. This will generally not exceed 10 wt.%.

The material of the other layer is characterised in that it will also be 15 a polyethylene, but now with a lower melting point, the difference being at least 10°C. Suitable polyethylenes are random or block ethylene copolymers, LLDPE, LDPE, VLDPE and the like.

For both types of layer materials it is to be noted that they will generally contain conventional additives, including but not limited to dyes and 20 pigments, flame retarders, UV-stabilisers, anti-oxidants, carbon black and the like.

In a less preferred option of the general approach to the present invention, each of the outer layers at itself consists of two or more separate layers. It is also possible that in the three-layer configuration (ABA), the two 25 outer layers have a slightly different composition.

The major part of the product of the invention consists of the central layer (B). In a preferred embodiment the amount of central layer is between 50 and 99 wt.%, preferably between 60 and 90 wt.%. The balance of the material consist of the outer layers (A).

In practice, the thickness of the tape, film or yarn will generally be up to 300, preferably between 25 and 300 μm . This is governed by the original film thickness and the stretch ratio, in this case the ratio of the speed of the stretch rollers. The width of the tapes can vary over a wide range, such as from 5 25 μm up to 50 cm or more. The width of the films can also vary over a wide range, e.g. from 1 cm up to 150 cm or more.

As indicated above, the material of the invention has very good mechanical properties. For example, the E-modulus will be at least 10 GPa, preferably at least 12.5 GPa. The tensile strength can easily be at least 0.25 10 GPa, even up to at least 0.4 GPa (value as measured by ISO 527). The upper limit for the strength that can be obtained in the materials of the present invention is about half of the theoretical value. This means that for polypropylene a value of 1 GPa and for polyethylene a value of 5 GPa will generally be the upper limit.

15 A film, tape or yarn according to the invention can be used to produce all kinds of materials, such as those discussed in the introduction.

One of the preferred embodiments of the use of the film according to the invention is the production of a reinforcing material for example by winding or stapling/stacking, and/or compacting it from the film. Preferably, 20 the material is then heat treated and pressed. By this heat treatment the individual films are welded together. In this way the structural integrity of the stapled/stacked material will be guaranteed. The said heat treatment will be done at a temperature between the softening point of the material of the outer layers (A) and the material of the central layer (B). A surprising property of 25 the heat treated material is the improved abrasion resistance and the resistance against delamination of the individual films.

During the heat treatment preferably a pressure is applied, in particular if the heat treatment involves subjecting a plate-like material or shaped article to a temperature at which the material of the central layer (B) 30 has a tendency to shrink (due to disorientation of the polymer chains to a more

random configuration). For example, polypropylene tends to shrink at a temperature above 100-115 °C. Preferably such a pressure is at least 5 bar. Very good results with respect to mechanical properties of the resulting materials have been obtained by compacting the material at a pressure in the 5 range of 20-70 bar.

Alternatively or in combination with applying a pressure, the material may be clamped during heat treatment, in order to avoid shrinking.

One of the preferred embodiments of the use of the tape or yarn according to the invention is the production of a (reinforcing) cloth for example 10 by weaving, winding, chopping and stapling, and/or compacting it from the tape, fibre or yarn. Preferably, the material is then heat treated and pressed. By this heat treatment the individual fibres are welded together. In this way the structural integrity of the cloth will be guaranteed. The said heat treatment will be done at a temperature between the softening point of the 15 material of the outer layers (A) and the material of the central layer (B). A surprising property of the heat treated material is the improved abrasion resistance and the resistance against delamination of the individual fibres.

The production of the material of the invention will generally be done by co-extruding the various layers. Generally cast extrusion is used, 20 whereby the extruder has a flat dye plate, without profile. When a film is manufactured the material may be stretched, after co-extrusion and cooling the material. In case a tape or yarn is manufactured, the material will be slit into the required width of the individual strands (after co-extrusion and cooling), followed by stretching.

25 The stretching can be a single stage or a multi-stage stretching. The stretch ratio in each step may be between 1.1 and 50 – preferably in the range of 2 to 10, more preferably in the range of 3 to 8 - the total draw ratio being important for determining the TSR, as defined herein. Very good results, with respect to mechanical properties of the stretched tape, yarn or film, have been

achieved in a multi-stage stretching process wherein the stretch ratio in the first stretching stage of the tape, film or yarn is 4-5.

It is preferred to stretch the material at a temperature between 20 and 250°C. Preference is given to stretching at a temperature below the DSC melting point of the material used for the central layer B (herein after "cold stretching"). Very good results have been achieved with a cold-stretching method wherein at least one of the stretching stages are carried out at a temperature below the DSC melting point of the outer layer, the temperature being in the range of 25-75 °C, more preferably between 30 and 60 °C

In case of multi-stage stretching, the first stretching is preferably carried out a relatively low temperature, more in particular in the range of 30-60 °C, and the subsequent stretching stage or stages are preferably carried at a relatively high temperature, for example at a temperature between 60 °C and the DSC melting point of the outer layer. Thus an a high as possible stretch can be achieved. Good results have been obtained with a subsequent stretching at a temperature of at least 100 °C. It is highly preferred to carry out the subsequent stretching at a temperature at which the stretch ratio until breakage (during the stretching process) is essentially maximised. It has been found that a temperature relatively close to the temperature at which the stretching is maximised, a film, tape or yarn is produced with very good mechanical properties, such as a very high E-modulus. The temperature at which the stretching is maximised can routinely be determined by the skilled person.

Between two stretching steps an annealing step may be included. This can also be done after the final stretching.

The material of the invention, both the individual films, tapes, yarns/fibres or a cloth or stapled/stacked material prepared thereof can suitably be used for incorporation in a matrix material, for example as reinforcing material. Examples thereof are various composite materials such as fibre reinforced plastics, automotive applications such as bumpers,

dashboards, engine covers and the like, application in the aerospace industry, such as construction materials for aeroplanes and the like. Other applications have been discussed here above.

The invention is now elucidated on the basis of the following
5 examples, which are not to be construed as limiting the invention.

Example 1

Using a co-extrusion line, a film was prepared consisting of a core
10 layer B of polypropylene having a DSC softening temperature of 152°C and two top layers A of a propylene random copolymer having a DSC softening temperature of 135°C (ABA-structure). The weight ratio A:B:A was 5:90:5.

The film was stretched at 55°C in a ratio of 1:5 followed by stretching at 128°C in a ratio of 1:3.4, thereby producing a stretched film that
15 had a stretch ratio of 1:17 and a thickness of 70 µm.

The elasticity modulus of the stretched film was 15.8 GPa and the strength was 585 MPa.

Example 2

20

Some of the films of Example 1 were processed into yarns of a width of 2.1 mm. The yarns were woven to produce a fabric material (tissue material), which was subsequently heat treated at 150°C to consolidate the structure. The final material had quasi isotropic stiffness of 7 GPa (determined
25 by ASTM 3039-76) and a tensile strength of more than 270 MPa. (determined by ISO 527).

Example 3

Some of the films of Example 1 were stapled/stacked and subsequently heat treated at 150°C to consolidate the structure. The final 5 material had quasi isotropic stiffness of 7 GPa and a tensile strength of more than 270 MPa.

Example 4

10 A film was prepared as described in example 1 except for the stretching stages being carried out at a temperature of 128 °C. The material (having a stretch ratio of 1:14 and a thickness of 70 µm) had an elasticity modulus of 11.5 GPa and a tensile strength of 450 MPa.

Claims

1. Monoaxially drawn polyolefin multilayer film, tape or yarn of the AB or ABA type, having a stretch ratio of more than 12, having an E-modulus of at least 10 GPa, substantially consisting of a central layer (B) of a polyolefin selected from polyethylene and polypropylene, and one or two other layers (A) of a polyolefin from the same class as the material of the central layer B, the DSC melting point of the material of the said other layers (A) being lower than the DSC melting point of the material of the said central layer (B), wherein the central layer (B) is between 50 and 99 wt.% of the material and the other layers (A) between 1 and 50 wt.%.
- 10 2. Film, tape or yarn according to claim 1, wherein the stretch ratio is at least 15, preferably at least 20.
3. Film, tape or yarn according to claim 1 or 2, wherein the stretch ratio is at most 50.
4. Film, tape or yarn according to any of the claims 1-3, wherein the material of the central and other layers is based on polypropylene.
- 15 5. Film, tape or yarn according to any of the claims 1-3, wherein the material of the central and other layers is based on polyethylene.
6. Film, tape or yarn according to any of the claims 1-5, wherein the material of the central layer is a crystalline polymer having a weight average molecular weight of at least 250 000 g/mol.
- 20 7. Film, tape or yarn according to any of the preceding claims wherein the outer layer or layers A at least consist of a random copolymer.
8. Film tape or yarn according to any of the preceding claims wherein the outer layer or layers A comprise a metallocene based homopolymer or
- 25 metallocene based copolymer.
9. Film, tape or yarn according to any of the claims 1-4 and 6-8, wherein the outer layer or layers A at least consist of a propylene ethylene

copolymer, having an ethylene content of between 1 and 25 mol.% and a propylene content of between 75 mol % and 99 mol %

10. Film, tape or yarn according to any of the claims 1-3 and 5-8, wherein the outer layer or layers A at least consist of an ethylene propylene copolymer, having an ethylene content of between 75 mol % and 99 mol % and a propylene content of between 1 and 25 mol.%

11-. Film, tape or yarn according to any of the preceding claims, having a thickness of between 25 and 300 μm .

12. Film, tape or yarn according to any of the preceding claims, having an E-modulus of at least 12.5 GPa.

13. Woven or non-woven composite prepared from a film, tape or yarn according to any of the claims 1-12, optionally having been heat treated.

14.. Composite material comprising a matrix material reinforced with film, tape or yarn according to claims 1-12, or woven or non-woven composite according to claim 9.

15. Method for manufacturing a monoaxially drawn polyolefin multilayer film, tape or yarn of the AB or ABA type having a stretch ratio of more than 12, wherein

(i) a film, tape or yarn of the AB or ABA type, substantially consisting of a central layer (B) of a polyolefin selected from polyethylene and polypropylene, and one or two other layers (A) of a polyolefin from the same class as the material of the central layer B, the DSC melting point of the material of the said other layers (A) being lower than the DSC melting point of the material of the said central layer (B), wherein the central layer (B) is between 50 and 99 wt.% of the material and the other layers (A) between 1 and 50 wt.% is provided by co-extrusion, and

(ii) the co-extruded film, tape or yarn is subjected to a single stage or multi-stage stretching at a temperature below the melting point of the central layer B.

16. Method for manufacturing a monoaxially drawn polyolefin multilayer film, tape or yarn of the AB or ABA type having a stretch ratio of more than 12, and an E-modulus of at least 10 GPa, wherein

5 (i) a film, tape or yarn of the AB or ABA type, substantially consisting of a central layer (B) of a polyolefin selected from polyethylene and polypropylene, and one or two other layers (A) of a polyolefin from the same class as the material of the central layer B, the DSC melting point of the material of the said other layers (A) being lower than the DSC melting point of the material of the said central layer (B), wherein the central layer (B) is between 50 and 99

10 wt.% of the material and the other layers (A) between 1 and 50 wt.% is provided by co-extrusion, and

(ii) the co-extruded film, tape or yarn is subjected to a single stage or multi-stage stretching.

17. Method according to claim 16, wherein step (ii) is at least partially

15 carried out at a temperature below the melting point of the central layer B.

18. Method according to any of the claims 15-17, wherein at least one of the stretching stages is performed at a temperature in the range of 25-70 °C.

19. Method according to claim 18, wherein the film, tape or yarn is first

20 stretched at temperature in the range of 25-70 °C and thereafter stretched at a higher temperature.

20. Method according to any of the claims 15-19, wherein a tape, film or yarn as defined in any of the claims 1-12 is prepared.

21. Tape, film or yarn, obtainable by a method according to any of the

25 claims 15-19.

INTERNATIONAL SEARCH REPORT

PCT/NL 02/00487

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/32 D01D5/253 D01D5/42 D01F8/06 B29C55/06
 B29C47/06 //D01F6/04, D01F6/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B D01D D01F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 578 370 A (FERRAR ANDREW N ET AL) 26 November 1996 (1996-11-26) cited in the application column 3, line 24 - line 58; example 1 column 6, line 1 -column 7, line 51; examples 4-6 --- EP 0 733 460 A (POLYMER PROCESSING RES INST ;NIPPON PETROCHEMICALS CO LTD (JP)) 25 September 1996 (1996-09-25) page 4, line 1 -page 7, line 26 page 9, line 49 -page 10, line 17 page 11, line 56 -page 12, line 5; examples 1-4; table 1 page 12, line 22 - line 47 page 15; example 9; table 2 page 16, line 30 - line 40 claims 1-16 --- -/-	1,2,4,7, 9,13-17, 20,21 1-6, 12-14,21
X		

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

° Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

PCT/NL 02/00487

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 366 210 A (SHELL INT RESEARCH) 2 May 1990 (1990-05-02) cited in the application page 2, column 2, line 23 -page 3, column 4, line 20 page 4, column 5, line 8 - line 44 ---	1-5, 7, 12, 15-17, 20, 21
X	GB 1 532 076 A (RUDIN A;KREIN H) 15 November 1978 (1978-11-15) page 3, line 57 -page 4, line 77; examples 1-5 ---	1, 3, 4, 11, 12, 15-17, 20, 21
A	GB 1 244 860 A (PHILLIPS PETROLEUM CO.) 2 September 1971 (1971-09-02) page 2, line 56 - line 70 claims 1-4, 12, 13; examples I, III, IV ---	15-20
A	EP 0 483 780 A (NIPPON OIL CO LTD ;NIPPON PETROCHEMICALS CO LTD (JP); POLYMER PROC) 6 May 1992 (1992-05-06) page 3, line 1 - line 41 page 8, line 37 -page 9, line 30 page 13, line 19 - line 38; examples 1-3; table 1 ---	1-3, 5, 6, 15-21
A	US 5 443 765 A (YOSHIMURA ISAO ET AL) 22 August 1995 (1995-08-22) column 13, line 52 -column 14, line 39 column 17, line 37 - line 47 column 69, line 51 -column 70, line 7 claims 1, 2, 5, 6 ---	15-21
A	US 6 071 598 A (WINTER ANREAS ET AL) 6 June 2000 (2000-06-06) column 2, line 32 -column 4, line 29 column 6, line 52 -column 8, line 65 column 9, line 39 - line 52 examples 5, 6 ---	1-4, 6, 8, 12-21
A	US 4 716 068 A (CRASS GUENTHER ET AL) 29 December 1987 (1987-12-29) column 6, line 40 -column 7, line 54; claims 1-18; examples 1-4 ---	1-21
A	US 5 302 453 A (KOUNO YASUO ET AL) 12 April 1994 (1994-04-12) column 5, line 4 -column 6, line 52 column 9, line 32 -column 11, line 11 examples 1-9; tables 1-3, 7-9, 11, 12 -----	1, 2, 5, 6, 12-16, 20, 21

INTERNATIONAL SEARCH REPORT
Information on patent family members

PCT/NL 02/00487

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5578370	A	26-11-1996	DE	513121 T1	22-07-1993
			AU	645526 B2	20-01-1994
			AU	7227091 A	21-08-1991
			CA	2100975 A1	03-08-1991
			EP	0513121 A1	19-11-1992
			WO	9111324 A1	08-08-1991
			JP	5504107 T	01-07-1993
			NZ	236960 A	27-04-1994
			ZA	9100730 A	27-11-1991
EP 0733460	A	25-09-1996	JP	8260232 A	08-10-1996
			JP	8260331 A	08-10-1996
			EP	0733460 A2	25-09-1996
			US	6054086 A	25-04-2000
EP 0366210	A	02-05-1990	US	5077121 A	31-12-1991
			AU	617549 B2	28-11-1991
			AU	4377589 A	03-05-1990
			BR	8905447 A	29-05-1990
			CA	2001556 A1	27-04-1990
			DE	68920545 D1	23-02-1995
			DE	68920545 T2	03-08-1995
			EP	0366210 A2	02-05-1990
			ES	2068886 T3	01-05-1995
			JP	2171241 A	02-07-1990
			JP	2894743 B2	24-05-1999
GB 1532076	A	15-11-1978	NONE		
GB 1244860	A	02-09-1971	BE	724832 A	03-06-1969
			DE	1812700 A1	28-08-1969
			FR	1604593 A	06-12-1971
EP 0483780	A	06-05-1992	JP	2938613 B2	23-08-1999
			JP	5214657 A	24-08-1993
			CA	2054427 A1	02-05-1992
			EP	0483780 A2	06-05-1992
			US	5578373 A	26-11-1996
US 5443765	A	22-08-1995	AU	647213 B2	17-03-1994
			AU	8872791 A	11-06-1992
			DE	69130860 D1	18-03-1999
			DE	69130860 T2	26-08-1999
			EP	0510213 A1	28-10-1992
			WO	9208611 A1	29-05-1992
			JP	5008356 A	19-01-1993
			JP	3122855 B2	09-01-2001
			US	5300353 A	05-04-1994
US 6071598	A	06-06-2000	DE	19519260 A1	05-12-1996
			DE	19548796 A1	03-07-1997
			AT	195285 T	15-08-2000
			AT	195286 T	15-08-2000
			AU	717450 B2	23-03-2000
			AU	5465296 A	12-12-1996
			AU	717639 B2	30-03-2000
			AU	5465396 A	12-12-1996
			AU	717318 B2	23-03-2000

INTERNATIONAL SEARCH REPORT
Information on patent family members

PCT/NL 02/00487

Patent document cited in search report	Publication date	Patent family member(s)		Publication date	
US 6071598	A	AU	5465496 A	12-12-1996	
		AU	717452 B2	23-03-2000	
		AU	5465596 A	12-12-1996	
		AU	717307 B2	23-03-2000	
		AU	5465696 A	12-12-1996	
		AU	720633 B2	08-06-2000	
		AU	5465996 A	12-12-1996	
		AU	717316 B2	23-03-2000	
		AU	5466096 A	12-12-1996	
		BR	9602539 A	27-10-1998	
		BR	9602569 A	06-10-1998	
		BR	9602574 A	06-10-1998	
		BR	9602576 A	06-10-1998	
		BR	9602577 A	06-10-1998	
		BR	9602578 A	06-10-1998	
		BR	9602580 A	06-10-1998	
		CA	2178104 A1	01-12-1996	
		CA	2178108 A1	01-12-1996	
		CA	2178109 A1	01-12-1996	
		CA	2178110 A1	01-12-1996	
		CA	2178111 A1	01-12-1996	
		CA	2178112 A1	01-12-1996	
		CA	2178113 A1	01-12-1996	
		DE	59605702 D1	14-09-2000	
		DE	59605705 D1	14-09-2000	
		EP	0747211 A1	11-12-1996	
		EP	0755779 A1	29-01-1997	
		EP	0747212 A1	11-12-1996	
		EP	0745477 A1	04-12-1996	
		EP	0745637 A1	04-12-1996	
		EP	0745638 A1	04-12-1996	
		EP	0745639 A1	04-12-1996	
		ES	2150615 T3	01-12-2000	
		ES	2150616 T3	01-12-2000	
		JP	9001649 A	07-01-1997	
		JP	9001650 A	07-01-1997	
		JP	9001651 A	07-01-1997	
		JP	9001652 A	07-01-1997	
		JP	9001653 A	07-01-1997	
		JP	9001654 A	07-01-1997	
		JP	9117994 A	06-05-1997	

US 4716068	A	29-12-1987	DE	3501726 A1	24-07-1986
			AU	589153 B2	05-10-1989
			AU	5250586 A	24-07-1986
			DE	3672262 D1	02-08-1990
			EP	0189066 A2	30-07-1986
			ES	551014 D0	16-04-1987
			ES	8705016 A1	01-07-1987
			JP	61168683 A	30-07-1986
			ZA	8600356 A	27-08-1986

US 5302453	A	12-04-1994	AU	642154 B2	14-10-1993
			AU	6129790 A	28-03-1991
			CA	2024944 A1	23-03-1991
			EP	0419060 A2	27-03-1991
			JP	4185709 A	02-07-1992
			KR	9300734 B1	30-01-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/NL 02/00487

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5302453	A	NZ 235403 A	26-05-1993
		US 5252394 A	12-10-1993
		CN 1050415 A ,B	03-04-1991
		JP 3034934 B2	17-04-2000
		JP 3279413 A	10-12-1991
		JP 2967935 B2	25-10-1999
		JP 3178418 A	02-08-1991